

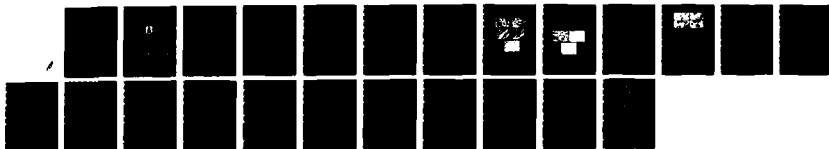
AD-A187 421

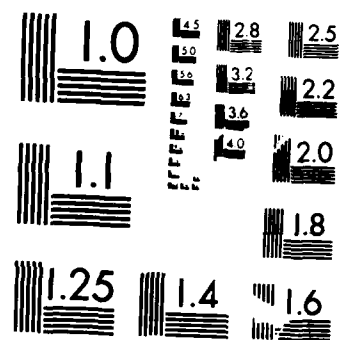
HIGH-MOLECULAR COMPOUNDS (SELECTED ARTICLES)(U) FOREIGN 1/1
TECHNOLOGY DIV WRIGHT-PATTERSON AFB OH 81 OCT 87
FTD-ID(R5)T-8858-87

UNCLASSIFIED

F/G 7/6

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

FTD-ID(RS)T-0850-87

AD-A187 421

FOREIGN TECHNOLOGY DIVISION



HIGH-MOLECULAR COMPOUNDS
(Selected Articles)



DTIC
ELECTE
NOV 09 1987
E

Approved for public release;
Distribution unlimited.



HUMAN TRANSLATION

FTD-ID(RS)T-0850-87

1 October 1987

MICROFICHE NR: FTD-87-C-000884

HIGH-MOLECULAR COMPOUNDS (Selected Articles)

English pages: 16

Source: Vysokomolekulyarnyye Soyedineniya, Seriya B,
Kratkiye Soobshcheniya, Vol. 12, Nr. 6,
June 1970, pp. 454-457; 2 Un. Nr; 463-466

Country of origin: USSR

Translated by: FLS, Inc.

F33657-85-D-2079

Requester: FTD/TQTR

Approved for public release; Distribution unlimited.

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WPAFB, OHIO.

TABLE OF CONTENTS

U.S. Board on Geographic Names Transliteration System	ii
Structural Changes and Physical-Mechanical Properties of Methylmethacrylate as a Result of Stretching Along a Single Axis, by A.N. Neverov, B.V. Perov, Yu. V. Zherdev	1
Polymerization of 2-Vinylbenzoyl Acid and its Byproducts, by G.M. Pogosyan, T.G. Karapetyan, S.G. Matsuyan	10

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



U. S. BOARD ON GEOGRAPHIC NAMES transliteration SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after Ъ, Ь; e elsewhere.
When written as Ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	\sinh^{-1}
cos	cos	ch	cosh	arc ch	\cosh^{-1}
tg	tan	th	tanh	arc th	\tanh^{-1}
ctg	cot	cth	coth	arc cth	\coth^{-1}
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
---------	---------

rot	curl
lg	log

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc.
merged into this translation were extracted
from the best quality copy available.

UDC 541.64:620.183

STRUCTURAL CHANGES AND PHYSICAL-MECHANICAL PROPERTIES OF
METHYLMETHACRYLATE AS A RESULT OF STRETCHING ALONG A SINGLE AXIS

A.N. ~~Ne~~verov, B.V. Perov, Yu.V. Zherdev

Stretching as a method of physical modification of the properties of polymers basic on the creation of a primary orientation of the macromolecules in the polymer material is a widely used technique, but the phenomena which take place during the orientation, particularly the processes of restructuring the supermolecular structure, especially in amorphous polymers have remained outside the field of view of researchers. In only one of the works of Zhurkov and his associates [1] were there presented data concerning changes in the supermolecular structure of PMMA [polymethylmethacrylate], but even in this work there was electron microscopic study of only the non-oriented polymer which had been stretched to its limits under test. *Russ. Rev. Phys. Chem.*

The intent of this research was to study the structure of the polymer at various stages of single-axis stretching, and also to locate

the mutual bonds between changes in the material's structure and its physical and mechanical properties.

We selected as the object of our research unplasticized and plasticized polymethylmethacrylate (PMMA) with 6% dibutyl phthalate in both non-oriented and stretched along a single axis at temperatures 20° higher than the polymer's softening point and a rate of stretching of 10-12 mm/min. From the sheets we obtained in this manner we prepared samples for testing mechanical properties and also for testing the structure of the materials. Testing of stretching and flexing were done with a rate of deformation of 0.7 mm/min on an Polyani-type advanced tearing machine with automatic registration of the deformation curves on an EPP-09 instrument. Testing for stretching were done of samples of the "two-sided paddle" type with an effective length of the working part of 18 mm, while testing of flexing was done at a temperature of -100° on frames measuring 4x6x70 mm. The value of the impact viscosity was determined by the Izod method on a "Dinstat" instrument at a temperature of 20° on frames measuring 4x5x15 mm. Study of the polymers' structure was done on a Telsa BS-242 electron microscope. We studied the chroma-angular reflections from the surface of chips of the samples, done along the surface of orientation at the temperature of liquid nitrogen.

In Figure 1 are presented electron microscope photographs of the surface of a chip of a sample of PMMA stretched to various levels of elongation ($\lambda = 1; 1.29; 1.59; 1.96; 2.50$). From the photograph it is easily seen that both in the unoriented ($\lambda = 1$) and in the oriented state the polymethylmethacrylate has a heterogeneous structure. In the stretching process there is orientation of randomly placed small fibrils along the direction of stretching, and the fibril structure appears less often. There is especially clearly expressed ordering stretching along the direction of orientation of the fibril structure as is seen (Figures 1d and 1e) in the highly oriented polymers ($\lambda = 1.96$ and 2.50). Hair-

like patches of fibrils have an average cross section measuring 300-400 Angstroms, and their length varies, in the highly oriented polymers reaching 0.1-0.3 microns.

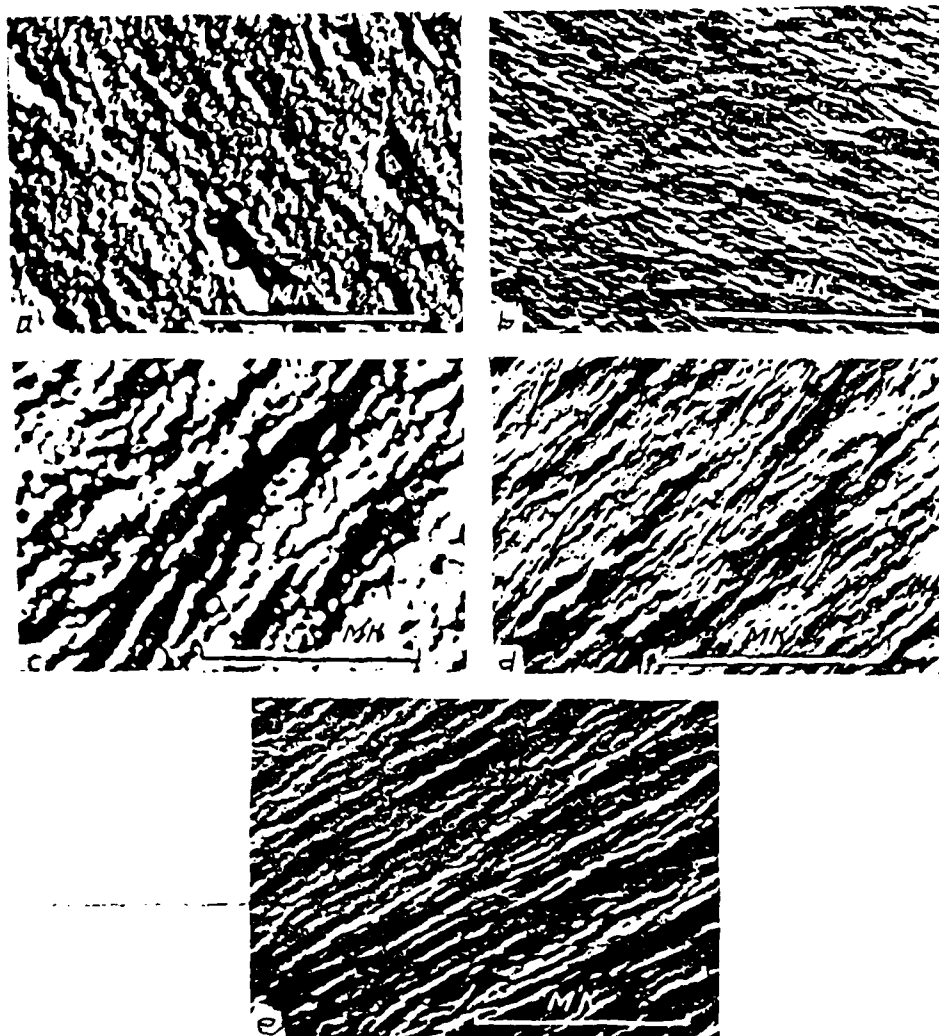


Figure 1. Electron microscope photographs of the surface of a polymethylmethacrylate chip.
 a - unoriented; oriented with λ : b - 1.29; c - 1.59; d - 1.96, e - 2.50

In the photographs it is easily noticeable that there is restructuring of the supermolecular structures as a result of the stretching, leading initially to some orientation of small supermolecular formations (Figure 1b), and then to enlarged structures (Figure 1c) and their further ordering in a position along the axis of stretching. Such a change in the supermolecular structure of the polymer as a result of the orientation leads to a quite significant change in its physical-mechanical properties. In figures 2 and 2 are presented data about changes in the mechanical properties of unplasticized polymethylmethacrylate as a result of stretching. The data presented demonstrates the varying character of the changes in various properties of polymers as a result of varying levels of orientation.

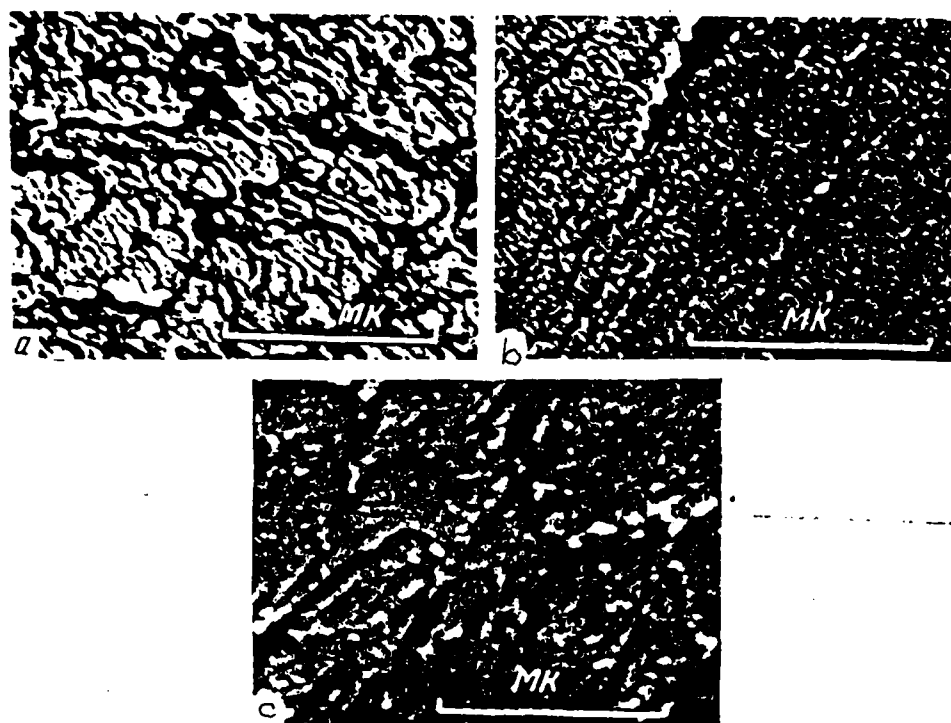


Figure 4. Electron microscopy photos of the surface of a chip of plasticized PMMA.

a - unoriented; uniaxially oriented, λ : b - 1.53; c - 1.96

Thus the strength indicators (specific impact viscosity, strength limit during stretching and flexing, sag) uniformly increase with an increase in the level of stretching, although the rate of increase of all these indicators at various stages of stretching are different. The value of the rupture elongation with an increase of the level of stretching passes through a maximum which is located in the area of stretching of $\lambda = 1.58-1.65$, which corresponds to the stage of the formation of microfibrils. Further increase in the level of stretching which leads to significant orientation of fibrils and their straightening, decreases the value of rupture elongation, apparently due to the attainment of a part of deformation capabilities of the molecules of the polymer when oriented.

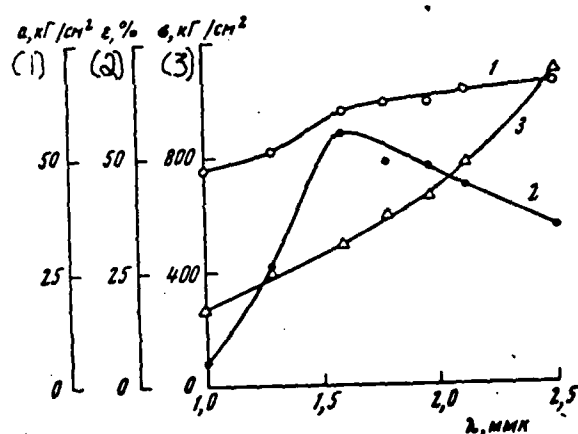


Figure 2. Mechanical properties of polymethylmethacrylate as a function of single-axis stretching with Temp 20° and λ :

1 - strength limit under stretching (σ); 2 - breakdown elongation (ϵ); 3 - specific impact viscosity (α)

Key: (1) α , kg/cm²; (2) ϵ , %; (3) σ , kg/cm²

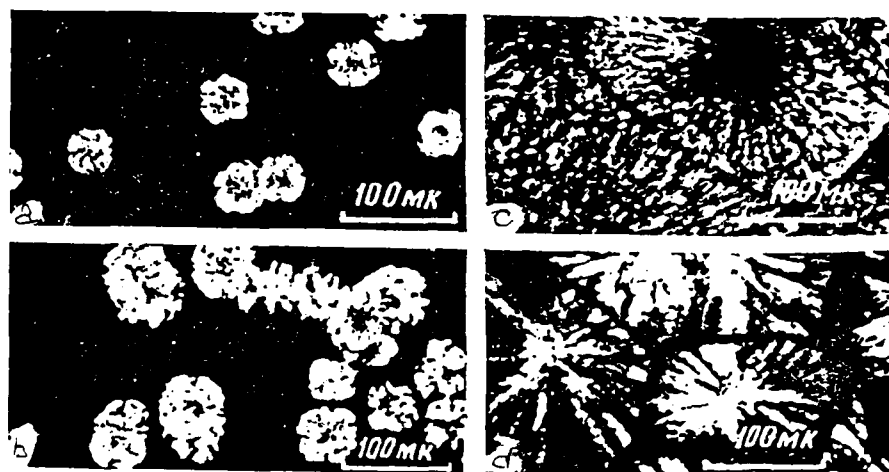


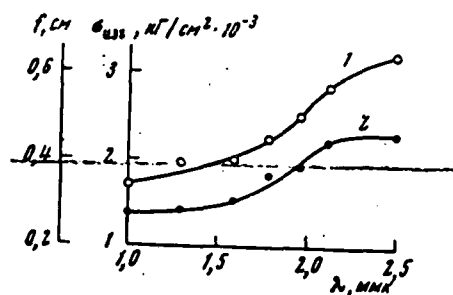
Figure 1. Microphotographs of the spherulite structure of samples of PS and PP

a - spherulite structures of partially spherulitized samples of PS; b,c - spherulite structures of PP and PS samples containing 3% respectively of atactic polymer

Key: mk = microns

Study of the structure of PMMA plasticized by dibutyl phthalate (Figures 4a, 4b) showed that in this polymer even in the unoriented state the supermolecular formations have a less clearly expressed character. In the electron microscope photographs there is noted a restructuring of the structure which takes place under the action of the orienting forces, but the oriented picture here is less clearly expressed in comparison with the analogous structure at the same levels of stretching for the unplasticized PMMA. Only at high levels of stretching ($\lambda = 1.96$) did we observe a relatively good formation of fibril structure which has, truly, and differing from the fibrils stretched to the limit, the presence of highly oriented unplasticized PMMA and less orderliness.

Figure 3. Strength under flex (1) and sag (2) of PMMA as a function of the level of single-axis stretching, λ at Temp -100° .



Such a less complete supermolecular structure apparently is due to the influence of the plasticizer which decreases the value of the intermolecular interaction and which complicates the formation of supermolecular structures with high orderliness, and also which facilitates the creep of structural elements during stretching, which significantly decreases the level of regularity of the polymer as a result of orientation. The character of the changes of the mechanical properties (along the axis of orientation) of the plasticized polymethylmethacrylate as a result of stretching (Figure 5) is similar to the changes in the ones for the unplasticized polymethylmethacrylate. For the plasticized polymer there is a characteristic uniform rather rapid growth in the value of the strength limit under stretching and the specific impact viscosity with an increase in the level of stretching, and the value of the breakdown elongation as a function of stretching is characterized by the presence of a maximum which is located at a level of stretching of $\lambda = 1.73$ -- that is, at a somewhat higher level of stretching than for the unplasticized polymer. This is in good agreement with the hypothesis about the lower value of orientation in the plasticized polymer at the same level of stretching.

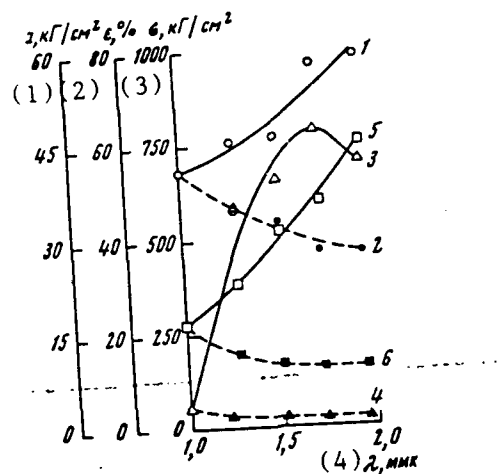


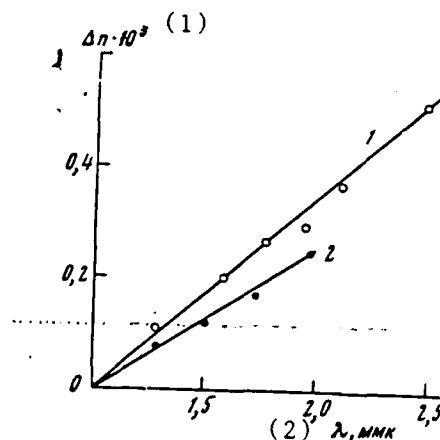
Figure 5. Mechanical properties of plasticized PMMA as a function of the level of single-axis stretching λ along the direction of orientation (1,3,5) and perpendicular to the direction of orientation (2,4,6)

1,2 - strength limit under stretch, 3,4 - break strength, 5,6 - specific impact viscosity

Key: (1) a , kg/cm²; (2) ϵ , %; (3) σ , kg/cm²; (4) λ , microns

Figure 6. The amount of birefringence in nonplasticized (1) and plasticized (2) PMMA as a function of preliminary single-axis stretching.

Key: (1) $\Delta n \times 10^3$; (2) λ , microns



The value of mechanical indicators of this polymer in the direction of perpendicular direction of stretching uniformly decrease with an increase in the level of orientation (Figure 5), which is evidently a feature of the growth and completion of the fibril structures when they are oriented due to further ordering of specific macromolecules and the less oriented structural elements. Such completion of the fibril structure and increase in the level of orientation of structural elements leads to a decrease of the reliability of the location of the chain molecules to the perpendicular direction of orientation and correspondingly to a decrease in the reliability of the value of the physical-mechanical indicators for the chemical bonds and an increase in the reliability of the less durable intermolecular (or more exactly the interfibril) forces.

Presented in Figure 6 are data on the character of changes in the value of birefringence of unplasticized and plasticized polymers which attest to the practically linear relationship between this value and the level of stretching and about the somewhat lower value for birefringence for the plasticized polymer in comparison with the unplasticized at the same level of stretching. Since the value of the birefringence of the

oriented polymer is to a substantial degree brought about by its structural elements (in particular, to the chained molecules), the presence of this relationship also attests to the increase in the orientation of structural elements of the polymers as there is an increase in the level of stretching of the polymer and of the lower amount of orientation in the plasticized polymer in comparison with the non-plasticized at the same level of stretching.

The authors express their gratitude to I.D. Deyev, N.I. Kondrateva, and T.N. Makashova for their help in conducting the experimental part of the work.

CONCLUSIONS

1. It was shown that single-axis stretching of polymethylmethacrylate is accompanied by the formation and strengthening of fibril structures and their orientation in the direction of stretching.
2. The orientation of the structural elements leads to an increase in the physical-mechanical properties of the polymer, from which there is more sensitivity to breakdown elongation under stretch, maximum value of which corresponds not to the stage of the greater level of orientation, but to the stage of the formation of macrofibrils.
3. The level of orientation of the structural elements in the plasticized polymer is less than in the non-plasticized at the same level of stretching.

LITERATURE

1. S.N. Zhurov, V.A. Marikhin, L.P. Romankova, A.N. Slutsker, *Vysokomolekulyarnyye soyedineniya*, Vol. 4., 1962, p. 282

UDC 66.095.26:678.746

POLYMERIZATION OF 2-VINYLBENZOYL ACID AND ITS BYPRODUCTS

G.M. Pogosyan, T.G. Karapetyan, S.G. Matsoyan

Institute of Organic Chemistry, Academy of Sciences, Armyanskaya SSR

Submitted 12 May 1969

Despite the large number of studies in the area of synthesis and polymerization of the byproducts of 4-vinylbenzoyl acid [1-4], 2-vinylbenzoyl acid and its byproducts have heretofore remained almost unexamined. We thought it was necessary to correct this oversight and to study the polymerization of the various byproducts of 2-vinylbenzoyl acid.

(1)

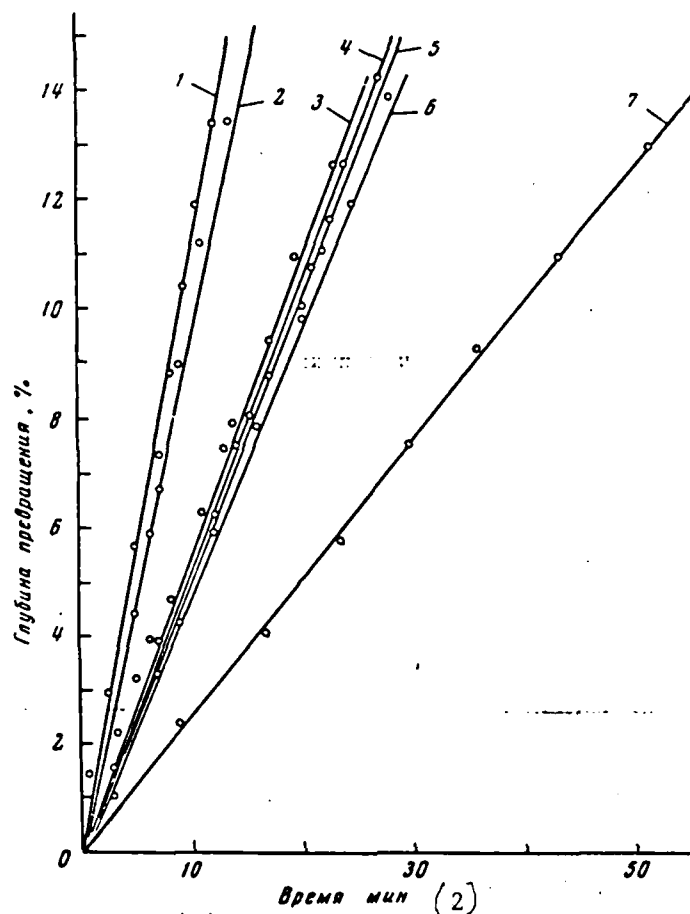
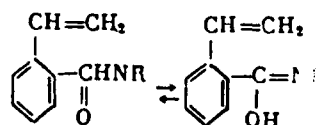


Figure 1. Initial rates of polymerization of 2-VBA and its byproducts.
1 - phenylamide, 2 - methanamide, 3 - methyl ether, 4 - amide, 5 - phenyl ether, 6 - 2-VBA, 7 - dimethanamide
Key: (1) - Amount of transformation, %; (2) - Time, minutes

Earlier we synthesized 2-vinylbenzoyl acid (2-VBA) [Soviet abbrev: 2-VBK] and some of its byproducts [5]. In this work we present the results of radical polymerization of 2-VBA, its chloro- anhydride, its methyl and phenyl ethers, its amide, and even the N-methyl-, N,N-methyl-, and N-phenyl- amides. Polymerization of these monomers was accomplished

in solution in the presence of 0.5 mole percent (of monomer) of dinitrile azoisobutyric acid (DAA) [Soviet abbrev: DAK]. The conditions of polymerization and also some properties of the polymers obtained are presented in the table. With the intent of comparing the reaction capabilities of the byproducts of 2-VBA, study of the polymerization was also done by the dilatometric method in a single molar solution in the presence of $5 \cdot 10^{-3}$ moles/liter of DAA at 80° . Polymerization of ethers of 2-VBA was accomplished in a solution of toluene, and the acid itself and its amides in a solution of dimethyl formamide. In analogous conditions for the chloro- anhydride of 2-VBA we did not manage to obtain reproducible results, apparently as a result of deactivation of the initiator under the influence of the highly-active chloro- anhydride group. When comparing the kinetic curves obtained (See Figure 1), it is seen that 2-VBA, its non-substituted amide, the methyl and phenyl ethers all polymerize almost at the same rate, while the substituted amides differ significantly from one another and form a series: phenylamide > methylamide > dimethylamide. It bears mention that the N-monosubstituted amides of 2-VBA are polymerized significantly faster than its ethers, non-substituted or disubstituted amides. The reason for this phenomenon, apparently, is the great tendency of the mono-substituted amides in comparison with the non-substituted amide to keno-enol tautometry:



The radical formed in enol form as a result of weak conjugating is less stable, and therefore, has a large capability to polymerize. Among the byproducts of 2-VBA that we studied, the highest rate of polymerization was observed in N-phenylamide, which tended more to form the enol.

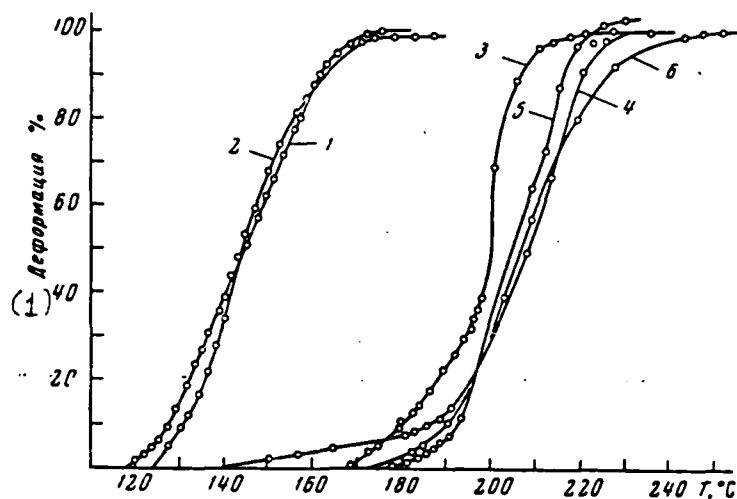


Figure 2. Thermo-mechanical properties of polymers of 2-VBA and its byproducts.

1 - phenol ether, 2 - methyl ether, 3 - 2-VBA, 4 - methanamide, 5 - phenylamide, 6 - dimethanamide.

Key: (1) Deformation, %

In Figure 2 are presented thermomechanical curves obtained for the polymers. The thermomechanical properties of purified samples of the polymers were obtained on an instrument designed by Tsetlin and his associates [6]. The polymers of 2-VBA and its amides have quite high heat resistance, and their glass point (T_g) is significantly higher than the T_g for polymers of the ether byproducts. We must note that we were unable to determine the T_g of the polymers of the chloro- anhydride and the non-substituted amide, since when we tried to determine them there was structuring and the formation of insoluble and non-melting polymers.

Polymerization of 2-VBA and its byproducts in 50% solution in dimethylformamide (DMFA) or in toluene (T) in the presence of 0.5 mole percent DAA (from the monomer) at 80°.

(Reaction duration was four hours)

$\text{CH}_2=\text{CH}$ $\text{C}-\text{R}$ O где R: (1)	Растворитель (2)	Выход полимера, % (3)	$[\eta]$ полимера, д.л./г (4)	T_g полимера, °C (5)	$\text{CH}_2=\text{CH}$ $\text{C}-\text{R}$ O где R: (1)	Растворитель (2)	Выход полимера, % (3)	$[\eta]$ полимера, д.л./г (4)	T_g полимера, °C (5)
	(6)					(6)			
OH	ДМФА	57,0	0,46	177	NH ₂	ДМФА	84,0	0,17	—
Cl	T	66,0	0,09	—	NHCH ₃	ДМФА	80,0	0,30	189
OCH ₃	T	69,0	0,14	130	N(CH ₃) ₂	ДМФА	36,0	0,12	190
OC ₆ H ₅	T	52,0	0,08	124	NHC ₆ H ₅	ДМФА	92,0	0,15	191

Key: (1) - where R; (2) - solvent; (3) Polymer yield, %; (4) $[\eta]$ polymer in dl/g; (5) T_g for the polymer in °C; (6) DMFA

The polymers of 2-VBA and its byproducts that we obtained were white powders. The polymers of the chloro- anhydride and the ether byproducts were soluble in aromatic and chlorinated hydrocarbons, and the polymer amides are soluble in dimethyl formamide.

Experimental Part

The monomers - 2-VBA and its byproducts - were synthesized according to the earlier described method [5]. Polymerization of monomers was done in ampules and dilatometrically in a toluene solution or a solution of dimethyl formamide. Measurement of the rate of polymerization was conducted in dilatomers with calibrated capillaries. The monomers containing the corresponding amount of initiator and solvent were preliminarily cleansed of dissolved gassed by freezing and thawing in a vacuum (10^{-1} - 10^{-3} mm). We filled the dilatometer in a deep vacuum, using

for this purpose a special unit ("grebenku" [probably a glass manifold]). The filled dilatometers were placed in a circulating oven in which the desired temperature was held with an accuracy of plus or minus 0.01-0.05°. The zero-state in the capillary was established at the moment of movement of the meniscus in a reverse direction (decrease in volume). The conversion factor for a given temperature was calculated by determining (by deposition) the amount of polymer which was formed in two parallel tests.

Measurement $[\eta]$ was conducted in a Ostwald viscosometer at 25° for a solution of polymers of chloro- anhydride and ethers in toluene and of 2-VBA and the amides in dimethyl formamide. To determine the Tg of the polymers obtained the desired load was equal to 0.34 kg/cm². The Tg was determined by extrapolation of the linear segment of the thermomechanical curve along the axis of the abscissa.

Conclusions

We conducted radical polymerization of 2-vinylbenzoyl acid and some of its byproducts in the presence of $5 \cdot 10^{-3}$ moles/liter of dinitrile of butyric acid at 80° in solution in toluene and dimethyl formamide. We established that under these conditions the 2-vinylbenzoyl acid, its non-substituted amide, its methyl and phenyl ethers all are polymerized at almost the same rate. The rate of polymerization for N-substituted amides were significantly different from one another and form the series: phenyl amide methyl amide > dimethyl amide. The hypothesis expressed that the reason for the high rate of polymerization of the N-monosubstituted amides of 2-vinylbenzoyl acid in comparison with other byproducts is the great tendency of the mono-substituted amides to keto-enol tautometry. We determined the characteristic viscosity and glass points for the polymers we obtained.

LITERATURE

1. C.S. Marvel, C.G. Overberger, J. Amer. Chem. Soc., Vol. 67, 1967, p. 2250; Vol. 68, 1945, p. 2106.
2. G.S. Kolesnikov, T.A. Soboleva, Izv. AN SSSR, Chemical Sciences Department, 1958, p. 760.
3. N.V. Adrova, K.K. Khomenkova, A.M. Dobnova, M.M. Koton, Zh. Obshch. Khimii, Vol. 32, 1962, p. 2267; Vol. 34, 1964, p. 1545; Sb. Karbotsepnyye vysokomolekulyarnyye soedineniya (Handbook of Carbon-Chain High Molecular Weight Compounds), Izdatelstvo AN SSSR, Moscow, 1963, p. 195.
4. G.M. Pogosyan, G.A. Zhamkochyan, S.G. Matsoyan, G.S. Kolesnikov, Izv. AN ArmSSR, Vol 18, 1965, pp 418, 421; Vysokomolekulyarnyye soyedineniya, Vol. 7, 1965, pp 707, 828; Vol. B9, 1967, p. 218.
5. G.M. Pozosyan, T.G. Karapetyan, S.G. Matsoyan, Zh. Organich. Khimii, Vol. 6, 1970, p. 139.
6. B.L. Tsetlin, V.I. Gavrilov, N.A. Velikovskaya, V.V. Kochkin, Zavodsk. Lab., Vol. 22, 1956, p. 352.

DISTRIBUTION LIST
DISTRIBUTION DIRECT TO RECIPIENT

<u>ORGANIZATION</u>	<u>MICROFICHE</u>
A205 DMAHTC	1
A210 DMAAC	1
B344 DIA/RTS-2C	9
C043 USAMIA	1
C500 TRADOC	1
C509 BALLISTIC RES LAB	1
C510 R&T LABS/AVRADCOM	1
C513 ARADCOM	1
C535 AVRADCOM/TSARCOM	1
C539 TRASANA	1
C591 FSTC	4
C619 MIA REDSTONE	1
D008 NISC	1
E053 HQ USAF/INET	1
E404 AEDC/DOF	1
E408 AFWL	1
E410 AD/IND	1
E429 SD/IND	1
P005 DOE/ISA/DDI	1
P050 CIA/OCR/ADD/SD	2
AFIT/LDE	1
FTD	
CCN	
NIA/PHS	1
LLNL/Code L-389	1
NASA/NST-44	1
NSA/1213/TDL	2
ASD/FTD/1QLA	1

END

FEB.

1988

DTic